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In atomic spectrochemical methods of analysis, the sample to be analyzed is decomposed into its constituent atoms and the atoms subsequently probed by atomic emission, absorption, or fluorescence. In such methods, it would seem to be straightforward to achieve extremely low detection limits, perhaps approaching the single-atom level, since atoms to be probed are in the vapor state, yield extremely narrow spectral lines, and should be relatively un-affected by other sample constituents. However, a number of factors conspire

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20. Abstract (continued)

to limit sensitivity and detectivity in atomic spectrochemical techniques.
Among these limitations are the relative inefficiency of most methods currently
used for forming the free atoms, the ordinarily brief time available for atom
observation which exists after sample decomposition is complete, and the
residual background signal which accompanies most atomic spectral measurements.
In this paper, a number of recent and proposed techniques to overcome these
obstacles will be reviewed and evaluated, with a view toward assessing the
present and future practicability of single-atom detection (SAD) methods
will be reviewed and new methods will be examined for improving the atomization
efficiency of real samples. Techniques for trapping ions or atoms for long-
term observation will be considered and methods for improving the selectivity
of atomic techniques will be assessed; these latter techniques are based
alternatively on spectral, temporal, or chemical characteristics of the
elements being sought.

APPROACHING THE LIMIT IN ATOMIC SPECTROCHEMICAL ANALYSIS

by

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INTRODUCTION

Selectivity and sensitivity are two of the principal goals of chemical analysis. In elemental analysis of chemical samples, the ultimate realization of these goals would involve the quantitative decomposition of a sample into its constituent atoms, which would then be sorted by element and counted individually.

Obviously, such a scheme is currently unrealistic. However, the recent introduction of high-power, wavelength-tunable lasers has spawned the development of a host of new methods which have been shown capable of single-atom detection (SAD). Although these methods are hardly ready for routine laboratory use, it is not unrealistic to extrapolate their application to real chemical samples.

In this paper, which is based on a presentation at the Spring, 1982 National Meeting of the American Chemical Society, methods for achieving single-atom detection will be reviewed, with greatest emphasis being placed on spectrometric (emission, absorption, fluorescence) monitoring techniques. Practical difficulties in applying the SAD methods to real samples will then be examined and ways of overcoming those difficulties evaluated. In particular, the practical impediment to achieving SAD in a real sample lies in the low efficiency with which such samples can ordinarily be dissociated into free atoms and the difficulty of distinguishing interfering signals from those produced by the resulting atom. Overcoming these obstacles will not be simple, but great promise lies in information which is now being obtained on the atom-formation process and in the development of new schemes for sample atomization. Also, differentiating between atomic and interfering signals will be simplified

by new approaches based on chemical or temporal characteristics of the atoms. Finally, techniques on the horizon which will enable the trapping of atoms or ions might allow their long-term observation and thereby enhance further one's ability to detect single atoms in complex chemical samples.

In order to assess the ability of present analytical methods to approach the SAD level, theoretical and experimentally determined detection levels will be presented for a number of chemical elements. A comparison of these methods will show that the most sensitive atomic spectrochemical technique currently available is based on emission from electrically generated discharges such as the inductively coupled plasma. However, such methods already approach their theoretical limits in terms of atomic detection and little further improvement can be expected. To approach more closely an SAD capability, laser-based techniques will have to be employed. Of the various laser-based techniques which are currently available, the most attractive from a practical point of view appears to be saturated laser-excited atomic fluorescence (LEAF).

METHODS FOR HIGH-SENSITIVITY
ATOMIC SPECTROCHEMICAL ANALYSIS

In atomic spectrochemical analysis, samples are partially decomposed into their component atoms and the atoms probed spectrometrically. As hinted in the introduction, such techniques seem almost ideally suited for SAD capability. However, a number of different atom-probing methods are possible and all do not have equal detection capability. In this section, the alternative schemes for detecting free atoms will be reviewed and their strengths

and limitations briefly assessed. Overall, the methods can be divided into those which detect ions or charged species and those which monitor atoms themselves. For an excellent review of these methods and their applicability to single-atom detection, the reader is referred to the paper by Alkamade (1).

Methods Based on Detection of Charged Species

Among the most sensitive of the techniques used for monitoring atoms are those which rely upon ionization. Included among such techniques are resonance ionization spectroscopy, commonly abbreviated RIS (2,3) and laser-enhanced ionization (LEI), which employs the so-called opto-galvanic effect or OGE (4). Because these detection methods are discussed in detail in other articles in this series, they will be considered only briefly here. The interested reader is referred to the papers by Hurst and Travis, respectively.

The principles involved in RIS and LEI are easily understood with the aid of Figure 1. In Figure 1 (and later in Figures 2 and 4) a solid arrow is employed to designate a radiational transition between energy states; an upward arrow indicates an absorption or pumping process whereas a downward arrow signifies loss of a photon through emission or fluorescence. In contrast, a transition indicated by a wavy line pertains to a radiationless process; an upward wavy arrow thereby indicates thermal activation thereas a downward wavy arrow indicates a loss of energy through collisional processes.

In the left side of Figure 1, the events occurring in RIS are diagrammed. In this method, an atom is ionized by absorption of a rapid succession of photons. The first photon (and possibly a second) is employed to promote the atom to a highly excited state, as close as possible to the ionization energy of the atom. Absorption of a final photon (or, in some cases simultaneous absorption of several photons) then raises the energy of the atom

beyond the ionization limit, causing spontaneous ionization. In RIS, detection of the resulting ion then occurs by cascade ionization of a gas-filled tube similar to those used in nuclear counting applications.

Clearly, the absorption of several photons required in the RIS process is a relatively improbable process unless the photon arrival rate (light flux) is very high. Consequently, RIS becomes feasible only when laser sources are employed. Moreover, the stepwise promotion of an atom to successively higher energy levels often requires more than one laser, at present a somewhat costly and experimentally tricky business. Nonetheless, RIS has been shown to be so efficient that it is in fact capable of single-atom detection. Essentially every atom which falls within the laser-irradiated sample volume then yields cascade ionization and a detectable current pulse. Unfortunately, the RIS sample chamber must be relatively clean and free from extraneous ions. As a consequence, it is difficult to volatilize into it real samples and no application of RIS to real samples has been reported to date.

Laser-enhanced ionization (LEI), like RIS, relies upon ionic detection. However, ions produced in the LEI method are generated by a partly thermal and partly radiative process. In particular, atoms residing in a relatively hot environment like a flame are always partly ionized. However, the fraction of the atoms which ionize is considerably increased if the average energy of each atom is raised. Obviously, such an energy increase is possible by exciting a fraction of the atoms; the greater the fraction, the greater the ionization. Accordingly, if one irradiates a group of atoms in such a hot cell, at a wavelength capable of being absorbed, an increase in the ionization of the atoms is observed. Detection of such ionization is possible simply by monitoring the resistance or conductivity of the atom-containing volume.

Because LEI can and in fact must be performed in a relatively hot or energetic medium, it is amenable to use in flames or plasmas of the kind commonly used in atomic spectroscopy (atomic absorption, plasma emission, etc.). In these applications, it has yielded extremely high sensitivity and a relatively high degree of selectivity. However, calculations indicate that LEI is unlikely to attain the sensitivity required by SAD.

Methods Based on Fluorescence, Absorption, and Emission

It is more common in the analytical laboratory to perform elemental analysis through emission, absorption, or fluorescence than by the ionization methods listed above. In fact, atomic absorption is still the most widely used technique for elemental analysis in the world. Energy-level diagrams displaying the three kinds of radiative measuring methods are shown in Figures 2 (fluorescence) and 4 (emission and absorption).

The fluorescence techniques can be divided into two categories involving, respectively, resonance and non-resonance transitions. A resonance transition is commonly considered to be one which involves the ground state of an atom. Consequently, resonance fluorescence involves an absorption from the ground state to an excited state and a subsequent return to the ground state by emission of a resonant photon of the same energy as that absorbed. In contrast, non-resonance fluorescence involves emission of a photon (fluorescence) of an energy and wavelength different from that absorbed. Several possible schemes for such an event are possible, of which two are diagrammed in Figure 2. In direct-line fluorescence, absorption of a photon raises an atom to a higher energy state from which fluorescence occurs. However, the lower level involved in the fluorescence transition lies above the ground state; return to the ground state following this emission process ordinarily occurs by means

of a radiationless (collisional) event. The difference in energy is then dissipated in the form of heat to the gaseous surroundings. Stepwise fluorescence, in contrast, involves emission of a fluorescence photon _after_ a radiationless event. Obviously, depending upon the arrangement of energy levels in a particular atom, either the direct-line or stepwise phenomenon would have highest probability and both can be used for high-sensitivity atomic detection.

Because the fluorescence radiation in a non-resonance process is at a wavelength different from that of the absorbed light, the method provides a higher degree of selectivity than resonance fluorescence. This enhanced selectivity is a result primarily of a greater ability to discriminate against scattered radiation. Understandably, scattered radiation will be at the same wavelength as the incident light; shifting of this wavelength in the non-resonance process enables the scattered radiation to be largely rejected.

The sensitivity of detection by either resonance or non-resonance fluor-escence is greatly enhanced by the use of an intense light source such a laser. At low incident light levels (irradiances), both kinds of fluorescence are directly proportional in intensity to laser power. Consequently, signals can be increased dramatically at the light levels of which a laser is capable. Moreover, at extremely high irradiance values, an even more practically useful phenomenon termed _saturation_ occurs.

During atomic energy-level saturation, the populations of an atom's upper and lower state are equalized as shown in Figure 3. To understand this process one must consider the events which lead to the population and depopulation of specific levels. Let us use the resonance fluorescence diagram on the left to illustrate. As laser radiation is incident upon a

group of atoms, a fraction of those atoms is raised (A) from the ground state
to an upper state; this fraction is increased as the irradiance on the atoms
becomes greater. At the same time, depopulation of the excited state occurs
by means of resonance fluorescence and, depending upon the atom's environment,
partially by collisional deactivation by neighboring atoms or molecules.
However, also shown in Figure 3 is the process termed stimulated emission, E,
which can occur to an atom in an excited state. Stimulated emission is iden-
tical to absorption, but is a downward transition. In particular, if a
resonant photon encounters an atom in an excited state, it has a high probability
of inducing the downward transition, causing the atom to emit a photon of
identical energy to the incident one. This phenomenon is, in fact, responsible
for laser action.

Of course, at low incident light flux, stimulated emission is a relatively
infrequent process, because of the low concentration of atoms which are excited.
However, as the incident light flux becomes greater and greater, an increased
number of atoms is pumped to the excited state and thereby are capable of
stimulated emission. Ultimately, at infinite incident light flux, the excited-
state population approaches that of the ground state, making upward and down-
ward transitions equally probable. Under these conditions, the radiationally
induced upward and downward transitions are exceedingly rapid and completely
outweigh the rates of either resonance fluorescence or collisional deactivation
of the excited state. As a result, under these so-called "saturation" con-
ditions, the excited-state population is determined entirely by the atom's
intrinsic properties and is relatively independent of the atomic environment.
Accordingly, quenching of the excited state becomes relatively unimportant,
the amount of resonance fluorescence seen from an atom is at its greatest

and, as shown in Figure 3, slight variations in incident laser power do not affect greatly the magnitude of the excited-state population. For these reasons, either resonance or non-resonance fluorescence measured under conditions of energy-level saturation is highly desirable from a practical standpoint. Under such conditions, laser power variations have relatively little effect and quenching conditions around an atom cause few errors. For these reasons, laser-excited atomic fluorescence (LEAF) obtained under saturation conditions is a prime contender for obtaining single-atom detection from real chemical samples.

Already, extremely low detection limits have been obtained by workers employing techniques such as non-resonance (5-8) or double-resonance (9) fluorescence spectroscopy. Importantly, such methods are amenable to use with conventional atomization devices of the kind commonly employed in plasma emission and atomic absorption spectrometry.

The absorption and emission processes are themselves indicated schematically in Figure 4. The principles behind these methods are well known and they are widely used in laboratories devoted to chemical analysis or to instruction. Consequently, they need not be discussed in detail here. For the present discussion, however, it is worth noting that atomic emission spectrometry from sources such as the inductively coupled plasma, microwave-induced plasma and dc plasma (10-14) provides some of the best detection capabilities for elements in real samples. Nonetheless, such techniques should fundamentally be less sensitive than those involving a fluorescence process, because of the impossibility of producing energy-level saturation in the atomic emission process. In brief, it is thermodynamically impossible to inject enough thermal energy into samples to saturate atomic energy levels; from the Boltzmann equilibrium,

the temperature required for saturation would be infinite. Similarly, sensitivity in atomic absorption measurements should be poorer than available from fluorescence techniques. Unlike emission or fluorescence, absorption methods require a measurement of small differences between two relatively large light levels (P_0 and P); drift or noise induced by the light source then precludes detection at anything approaching a single-atom level. These points are lucidly discussed and amplified in the excellent article by Alkemade (1).

To indicate the current state-of-the-art for elemental detection in real samples, the paper by Bolshov, et al. (6), should be consulted. In that study, the authors showed it was possible using saturated LEAF to detect as few as 1300 Pb atoms/cm^3. Non-resonance fluorescence from the lead atoms was observed at 405.8 nm and the atoms were produced from lead salts in a graphite furnace similar to the kind commonly employed in "non flame" atomic absorption spectrometers.

Impressive as the detection limits cited by Bolshov, et al. might be, they are far removed from the single-atom level. Moreover, as will be shown later, similar detection capability exists for few other atoms, making the technique limited in scope. It is appropriate, therefore, to consider in detail the factors which hinder the development of ultra-high-sensitivity atomic methods of analysis. These hindrances and possible ways of overcoming them are outlined in the next section.

SAD IN REAL CHEMICAL SAMPLES

As shown by Bolshov, et al. (6), it is possible to detect lead by saturated non-resonance LEAF at nearly the single-atom level if one employs as an

atom cell a heated quartz cuvette containing gaseous Pb atoms. However, detectivity is appallingly degraded when real chemical samples (Pb salts) and conventional atom-generation devices (carbon furnaces) are utilized. This loss in capability arises principally from two factors--the inability to atomize completely a chemical sample and the difficulty in distinguishing spectroscopically between the liberated atoms and their environment. In the case at hand, Pb atoms in a quartz cuvette are isolated completely and can be atomized at known concentrations for a given cell temperature. Moreover, fluorescence from the atoms can be viewed against the negligible cell background. In contrast, Pb atoms liberated from a salt are released with poorer efficiency. In addition, those atoms which are liberated must be viewed against the background of the incandescent carbon furnace and the possible flickering of the laser source caused by convection within the hot chamber.

Keys to ultra-high sensitivity detection in atomic spectrometry then seems to reside in improved sample atomization and the ability to discriminate between liberated atoms and potentially interfering signals. In addition, improved sensitivity should be derived from the ability to observe an atom for an extended period of time; under saturation conditions, the atom will emit as many as 10^8 photons per second. Let us consider first means by which samples might be more efficiently atomized.

Sample Atomization -- The Key to SAD

Steps ordinarily followed in converting a sample to free atoms are diagrammed in Figure 5. In most analytical schemes, a solid sample is first dissolved to form a solution which can, alternatively, be sprayed into a flame or plasma or be deposited in a heated cuvette or furnace. In a flame or

plasma, droplets in the spray are evaporated (desolvated) to form tiny
solute particles which then must vaporize to form the free atoms or ions
necessary for an analysis. Similarly, a dried solute deposit present in
a furnace or other electrothermal atomizer must be dried and thermally
vaporized. In either kind of atomizer, the sample vapor will consist of
atoms, molecules, ions, and molecular fragments and will be accompanied
by components from the atomizer (flame, plasma, etc.) itself. Accordingly,
the atoms or ions which are probed for analysis are ordinarily only a small
fraction of the original sample constituents and, as importantly, are accom-
panied by potentially troublesome foreign molecules.

To improve the overall efficiency of atomization, several alternative
approaches are possible. In the most elegant approach, each of the events
outlined in Figure 5 would be understood in detail, enabling the factors
affecting it to be controlled and atomization thereby optimized. At the
other extreme, a brute-force approach might be taken and each sample brought
to a temperature high enough to insure complete atomization. Alternatively,
new, high-efficiency atomization devices might be sought whose action is
capable of gently but thoroughly atomizing a sample.

All three of these approaches are feasible and each is being pursued
in laboratories around the world. Although coverage of these many studies
could not be attempted here, representative examples will be given from a
number of investigations.

Understanding Atom Formation. A great deal of effort has been expended
over the last two decades in understanding atom-formation processes in sources
used for atomic spectrometry. Particularly noteworthy are the work of Walters
(15,16) on the high-voltage spark and those of L'Vov (17) on the carbon furnace

atomizer. Because of major differences in the construction, design, and utilization of specific atomization devices, investigations tailored to understand each one are quite different and the findings difficult to discuss in a brief summary. To illustrate the scope, complexity, and current state of such investigations, the author has chosen an example from his own laboratory. In this example, events leading to atom formation in analytical flames and plasmas are examined.

In most flames and plasmas of the kind used in atomic absorption or emission spectrometry, samples are introduced in the form of an aerosol; each aerosol droplet must then undergo the sequence of events outlined in Figure 5. Unfortunately, a wide range of droplet sizes is produced and droplets travel an erratic path to and within the flame or plasma, making a detailed study of the events occurring to a single droplet almost impossible. To circumvent these difficulties, a device was developed (18,19) which enables individual droplets to be sent along a prescribed, reproducible trajectory in a flame. The photograph of Figure 6 shows this device in operation. Figure 6 reveals a single-flash photograph showing a stream of droplets being sent into a stable air-acetylene flame at the rate of approximately 1000 per second. However, because of the stability of the droplets and the flame itself, the photograph could also represent the sequence of events which occurs to a single droplet as it travels within the flame. From the photograph, it is apparent that droplets evaporate as they pass upward in the flame, to form a tiny solute particle which then begins to vaporize, releasing a luminescent plume as it travels. With such an arrangement, all the events outlined in Figure 5 are separated temporally and spatially and can be examined on an individual basis. From such investigations, the mechanism of each atomization step can be studied and, hopefully, optimized.

Unfortunately, the current state of knowledge concerning atomization in flames, plasmas, furnaces, and electrical discharges is meager, despite the effort being invested. As a result, major improvements available from a rational understanding of atomization processes are unlikely to occur in the near future. Rather, this rational approach to improving atomization is directed at long-term achievement. Nonetheless, information which has already been gleaned about atomization has made it possible to effect significant improvements in existing analytical sources; hopefully, these investigations will be expanded by new workers entering the field.

Brute-force Atomization. When one considers recent technological achievements and such endeavors as the attempt to control and confine thermonuclear reactions, the concept of atomizing a sample completely seems not far-fetched at all. In fact, the total amount of energy required to fully atomize a sample can be calculated to be rather small. However, the effective temperature required to perform such a feat is considerable, especially if the feat is to be achieved on a time scale convenient for chemical analysis.

Clearly, there would be few advocates of employing a controlled thermonuclear reaction as an atomization source for atomic spectrometry. However, some of the most successful approaches to high-sensitivity atomic methods have relied upon thermally hot sources for both atom-formation and excitation. Perhaps the most successful such source is the now widely used inductively coupled plasma (ICP). The construction and operation of an ICP can be understood with the aid of Figure 7. In this diagram, it can be seen that the inductively coupled plasma is simply a hot, partially ionized gas (usually argon) supported by a high-power (2 kW) radio-frequency field. The field is produced by a coil which surrounds the outer quartz tube which contains

the plasma gases. By inductive coupling, the field accelerates electrons within the gas, which then collide with argon atoms and ionize them. The electrons released by the ionization process are then themselves accelerated to produce further ionization. The final result is a plasma which reaches a maximum temperature of approximately 10,000° C and into which sample sprays can be introduced. In the plasma, this spray undergoes the events outlined in Figure 5 to yield a fairly high fraction of free atoms and ions which can then be viewed by emission. Because of the high temperature available in the ICP, atomization is relatively complete, so that interferences are small and sensitivity is high; sensitivity is further increased by the high temperature at which emission is generated. As will be shown later, these attributes make the ICP one of the most sensitive of all current methods for atomic detection.

Unfortunately, the ICP has a number of drawbacks as well, particularly in its application to single-atom detection. For example, the spectral background produced by the hot plasma gases is rather high, even at regions far downstream from the location where the plasma is initiated. In addition, at the high temperatures encountered in the ICP, ionization of many elements is extensive, particularly for the alkali and alkaline earth metals. Importantly, singly ionized atoms of the alkaline earths have electronic structures similar to those of neutral alkali metal atoms, suggesting their strong emission characteristics. For this reason, alkaline earth metals are ordinarily observed by means of their ionic emission spectra. In fact, alkaline earth ionic emission is often so strong that it is scattered within the monochromator or spectrometer used to separate elemental emission lines; this scattering can then generate an erroneous signal for other elements.

Frequently, this sample-generated background spectrum is even more serious than the background caused by the plasma itself. Accordingly, it is ordinarily necessary in ICP spectroscopy to employ a fairly high-resolution detection system and to scan carefully across elemental emission lines to resolve such lines from a continuous background level.

Other factors which limit the application of the ICP to SAD are the flickering noise present in the source, the large number of charged species it contains, and the degree of sample dilution which occurs. Flicker noise is simply the long-term drift which exists in many atomic spectrometric sources. Unfortunately, this flicker causes variations in the atomic (elemental) signal as well as in the background and therefore makes it difficult to detect single atoms. Also, the large flow rate of argon gas necessary to support the ICP (15-20 L/min) yields an enormous dilution of atoms formed from a particular sample. A rough figure-of-merit is that 1 μg/ml of sample in solution yields approximately 10^{10} atoms/cm^3 in the plasma. The consequence of this dilution is, obviously, reduced detection capability. Finally, because the plasma itself is charged and produces from the sample a larger number of charged species, it is not ideally suited to SAD methods which rely upon ion detection (RIS or LEI).

Of course, the ICP is convenient to use as an atom reservoir for atomic fluorescence measurements and several publications have dealt with such an approach (20,21). In fact, one commercial instrument has already been introduced which employs the ICP in an atomic fluorescence mode (22). However, recent calculations show (23) that detection power in the ICP is already near its theoretical limit so that little improvement can be expected in the future. This point will be amplified later.

New, High-Efficiency Atomization Methods. Perhaps the most promising
approach for near-term improvements in sample atomization lie in the develop-
ment and utilization of new atomization devices themselves. Ideally, such
devices should be designed with a state-of-the-art knowledge of atomization
processes, as discussed earlier. Also, because such sources of atoms for SAD will
probably have to rely upon fluorescence or ion detection for sensitivity,
they can be designed with relative freedom from constraints which led to
the development of sources like the ICP, where both atomization and excitation
must be performed.

In the design of such atomization devices, some direction might be
obtained from already successful techniques for SAD. In the main, successful
methods have relied upon a thermal generation of atoms from relatively
volatile elements; the released atoms were then held in a relatively quies-
cent environment so that atom probing time could be increased. Unfortunately,
many samples, indeed many elements, are not readily vaporized or fully
atomized at temperatures conveniently obtainable in the laboratory. For
many others, of course, high-temperature furnaces might suffice. It will
be shown later that some of the highest detection capability for real samples
is, in fact, available using furnace atomizers. For those elements or
samples which are not conveniently atomized even at furnace temperatures,
an alternative approach might be sought. Of those which are currently
available, the most promising such approach appears to be one involving
ion sputtering.

Ion sputtering can be understood with the aid of Figure 8. To employ
sputtering, a sample must be conductive or be made to be conductive by
admixture with a suitable material (probably graphite). The sample is

then enclosed in a chamber which is filled with several Torr of an inert
gas, probably Ar or Ne. Next, the sample is held at a relatively high
negative voltage (500 V) with respect to a distant anode and a current of
between 5-300 mA is allowed to pass between the electrodes. As a result
of this current flow, positive ions of inert gas are generated which are
then attracted strongly to the cathodic (negative) electrode surface.
Bombardment of the surface with the inert gas ions then fragments the surface.
Importantly, the fragments are largely in the form of atoms, which then
form a relatively dense cloud above the sample surface and which would be
useful for SAD.

The attributes of the sputtering method are many. First,
it is an "outside-in" process, in that atoms are sputtered from the surface
layers of the sample; the sample is then eroded gradually, enabling atom
concentrations at various depths to be monitored. This "outside-in" char-
acteristic also prevents explosive sample fragmentation, which can occur
in many thermal volatilization schemes. Second, atoms are generated with
high efficiency, with little molecule formation occurring. Finally, atoms
are generated in a quiescent environment, enabling them to be probed over
long periods of time and thereby enhancing detectivity. Of course, sputtering
has its drawbacks as well. It is a relatively slow process, often requiring
several minutes to develop a stable population. Also, samples must be con-
ductive, must be held within a closed chamber, and the chamber must be evacu-
ated. This latter disadvantage is probably the most serious from a practical
standpoint.

Fortunately, sputtering can also occur at atmospheric pressure, thereby
simplifying instrumental and experimental procedures. A photograph of a
sputtering discharge operating at atmospheric pressure is shown in Figure 9.

This device, termed a "microarc", has many of the characteristics of a con-
ventional sputtering discharge, but works more rapidly because of its atmos-
pheric-pressure operation. Consequently, samples need not be handled in
vacuum and they are atomized much more quickly than at reduced pressures.
In addition, even non-conductive samples can be atomized using the microarc;
it is necessary only to deposit a solution containing them on a conductive
substrate. Tungsten wires are usually employed for this purpose.

Although the microarc has not yet been applied to SAD, it has been
coupled to other atomic spectrochemical excitation sources, particularly
the ICP and the microwave-induced plasma (MIP) (24-26). The MIP, unlike the ICP,
dilutes the atoms less, operates at higher frequency, lower powers and inert gas
flows, and has greater excitation capability than the ICP. However, also unlike
the ICP, the MIP atomizes samples inefficiently. A marriage of the microarc and
MIP therefore seems particularly appropriate. The sensitivity of the microarc-
MIP combination will be illustrated in a later section.

Increasing Atom Residence Time

No matter what kind of atomization device is ultimately adopted, one
of the keys to SAD lies in the ability to probe sample atoms for an extended
period of time. If ion detection is employed, such extended probe times
would increase the efficiency of ion production and thereby insure that
each atom can be detected. Similarly, in an atomic fluorescence scheme,
the ability to observe an atom for extended periods of time yields a greater
signal. In fact, if extended atom observation times are available, fluores-
cence should be the more sensitive of the two methods. As indicated earlier,
under conditions of saturation, each atom would yield approximately 10^8
photons per second, so that the extended viewing times would help to dis-

tinguish atom-generated fluorescence from any background.

Several arrangements for trapping atoms or ions might be envisioned. In the simplest arrangement, such as those found in sputtering or thermal vaporization schemes, the atoms would be held within a closed chamber, possibly at reduced pressure. However, as mentioned before, such a method would be experimentally inconvenient. Alternatively, atoms could be heated within a semi-enclosed volume, such as a tube, and allowed to slowly escape from the tube. Although observation times would then be shorter than with an enclosed vessel, many more samples could be examined over an available time period. Finally, entirely new schemes for atom or ion trapping could be devised.

The second of these approaches is embodied in the carbon furnace often used for atomic absorption spectrometry. Basically, such a furnace consists simply of a carbon or metal tube, which is heated resistively. As suggested earlier, the increased atom observation times available with a tube furnace have yielded exceptional detection limits, but are still far short of SAD capability. Nonetheless, optimization of such a tube furnace for SAD applications should improve its utility markedly; it can be anticipated that a number of such applications will appear in the literature in the next few years.

More satisfying would be the development of methods for the long-term trapping of atoms or ions. Under ideal conditions, one could envision atoms or ions being trapped for minutes, hours, or days, enabling them to be examined at leisure. Under such conditions, it should be possible to identify all the elements in a chemical sample and to quantitate elemental concentrations by counting atoms as they pass the observation beam. If ion

detection were employed, each atom would then be counted individually. In
contrast, atomic fluorescence detection would enable each atom to be "counted"
many times to yield sensitivities conceivably surpassing the single-atom
level.

What might the nature of such an atom or ion trap be? Surely, if
physicists are capable of confining, even briefly, extremely high-tempera-
ture plasmas of the kind found in fusion reactions, it should be possible
to confine a relatively low-temperature gas such as would be produced by
atomization devices of the kind mentioned earlier. However, the complexity
of such a confinement device would have to be reduced substantially for it
to become practical in routine chemical analysis.

As a first step to such a confinement procedure, a "linear" ion trap
might be employed. In a linear trap, ions would be confined to motion
along one axis, enabling them to be simply probed with a laser. Conveniently,
such trapping can be accomplished using a component of a quadrupole mass
spectrometer (27).

Specifically, the mass analyzer in a quadrupole spectrometer consists
simply of four rods which are driven by a radio-frequency electric field.
The result of this field is to create a potential well in the very center
of the rod array, so that ions present between the rods are re-focused in the
center of the array even when driven off center by thermal motion. Accordingly,
ions traveling through the quadrupole unit reside almost exclusively along
a line lying in the very center of the four-rod arrangement. Probing the
ions with a laser should then be relatively simple. Significantly, this
scheme has already been applied in atomic detection (28-30) and is likely to receive
further attention in the future. Of course, it has the principal drawback

of requiring ions for observation, thereby precluding the use of ionization techniques and limiting the application of the method to those atoms which have spectroscopically (by fluorescence) accessible ions.

Increasing Selectivity for SAD

Because background radiation, ionization, etc. sometimes precludes single-atom detection, approaching the limit in atomic spectrochemical analysis might be possible only if methods for increasing selectivity can be found. In the case of ion detection, such selectivity must be found in both the method used to generate ions and in the detection process. If atomic fluorescence monitoring is selected, both excitation and fluorescence processes must be rendered more specific. Conveniently, ion generation by either RIS or LEI or the excitation required in fluorescence are possible using modern, extremely narrow-band dye lasers. Monochromaticity of these lasers is often sufficient to insure selective excitation not only of atoms of a single element, but even of specific isotopes of that element. This capability is at the heart of many modern isotope-separation proposals. However, secondary ionization (in ion detection) or background radiation (in fluorescence) can still cause errors even when laser excitation is employed, requiring that additional selectivity be incorporated into any SAD scheme.

Unfortunately, incorporating additional selectivity in ion detection (such as by the incorporation of a mass spectrometer) unavoidably reduces detection efficiency. Also, because conventional ion-detection arrangements are ordinarily destructive, each ion can be detected only once. The reduced efficiency associated with increased selectivity in ion detection would therefore probably drop the method below the level of single-atom detectability. Accordingly, it would seem that ion-measurement-based SAD schemes are unlikely

to be applicable in the future to a wide variety of "dirty" chemical samples.

In contrast, fluorescence detection enables each atom to be examined many times, as mentioned earlier. Accordingly, a tradeoff between selectivity and sensitivity can be tolerated in LEAF, even for real chemical samples. Significantly, several directions might be taken to improve LEAF selectivity; these directions would employ, respectively, the wavelength, time characteristics, and polarization of fluorescence.

The most straightforward example of the wavelength selectivity available in LEAF is the use of non-resonance transitions, as outlined earlier. It will be recalled that non-resonance fluorescence lies at a wavelength different from that of the exciting source beam, so that discrimination against scattered radiation is possible. However, it would seem initially that distinguishing between different kinds of atoms using LEAF would be possible only through use of an extremely high-resolution monochromator. Even then, the line widths exhibited by many atoms, especially in the hot environment of, say, a carbon furnace, might cause spectral overlap between fluorescence lines of different elements. Moreover, broad-band background emission which often accompanies many atomization devices would in some situations render SAD impossible.

However, resolution in LEAF need not be limited to that available from a spectrometer. For example, improved selectivity could be obtained using the scheme outlined in Figure 10. In Figure 10, selectivity is enhanced by use of two lasers and two sequential transitions within a given atom. The first laser (L_1) excites the atom to a first (resonance) level, after which a second laser (L_2) promotes the atom to an even higher state, from which fluorescence occurs. In a proposed experimental arrangement, one of the lasers would be "on" continuously while the other one would be pulsed. Monitor-

ing fluorescence at the pulsing frequency would then distinguish between
the desired fluorescence signal and that from any other atom which happened
to possess even one energy level common with the element sought. Two-laser
schemes of this kind are capable of almost incredible spectral resolution,
exceeding even the Doppler limit (31).

It should be possible to improve specificity also by chemical means.
In the simplest chemical approach, elements would be separated from each
other prior to atomization, thereby avoiding any potential interferences.
However, it should be possible also to modify the atmosphere within an
atomizer vessel to selectively "scavenge" undesired atoms and thereby avoid
their detection. Similarly, by judicious choice of discharge gases (for
example, He, Ar, or Ne) it should be possible to avoid many spectral inter-
ferences.

Finally, specificity could be enhanced by employing time as a variable.
For example, in a thermal atomizer, such as a carbon furnace, different
compounds will be volatilized at different temperatures. Therefore, if
a temperature ramp would be employed in such an atomizer, it should be
possible to avoid many potential interferences on the basis of the atomi-
zation or "appearance" time of each kind of atom (32).

On an even faster time scale, it should be possible to isolate fluores-
cence from scattered radiation or to distinguish between different elements
whose atoms emit at adjacent wavelengths. The basis for this method would
lie in the fact that each atom possesses an intrinsic excited-state lifetime.
Accordingly, atoms which are excited by a laser pulse would then experience
a transient excited-state over-population, from which first-order kinetic

decay would occur. This decay occurs at a rate characteristic of a particular atom. Therefore, it should be possible to distinguish different atoms from each other partially on the basis of time resolution. Perhaps more importantly, it is possible (33) to distinguish between scattered radiation and true fluorescence on a temporal basis, since scattering is an instantaneous process. To achieve such selectivity, it would be necessary only to use a very short pulse from a laser and to delay observation of the atomic fluorescence until the laser pulse (and therefore scattering) has terminated. This process is illustrated in Figure 11.

CURRENT STATUS

From the foregoing narrative, it is clear that a number of experiments are currently underway which should enhance our ability to perform SAD on real samples. However, no such complete methods currently exist. In this section, an attempt will be made to evaluate the current state of atomic detection in spectrochemical analysis and to assess the degree to which SAD seems feasible.

To begin, it seems appropriate to examine how closely current atomic methods approach ideality. That is, it is possible using theoretical models to estimate the limit of detection (LOD) of essentially any atomic spectrochemical technique; this approach has been elegantly explained by Winefordner, et al. (23,34,35). To formulate such a model, estimates or measurements are made of the degree to which a particular analytical technique generates free atoms from a sample. Instrumental limitations in the technique are then evaluated in an effort to determine the limiting "noise" source. This limiting noise is the source of greatest imprecision in the method and

thereby governs the lowest concentration of an element which can be measured. The final consideration required in the models is the magnitude of signal to be expected from a particular kind of atom. The signal can be predicted on the basis of a knowledge of the atom's fundamental characteristics and the properties of the detection method. For example, in the case of emission measurement, a signal would be related to the temperature of an excitation source, the efficiency of collection of emitted radiation, and the transition probability of the atom being examined.

Under optimized (sometimes idealized) conditions, limiting noise sources will ordinarily be those produced by a photon detector. Because such a detector responds to the arrival of individual photons, its output is inherently noisy, because of the random photon arrival time. Depending on whether the photons arise from the desired atoms themselves or from a background source, the situation is said to be "detector shot noise limited" or "background shot noise limited", respectively. In the case of an absorption measurement, where an auxiliary source is employed, the measurement is said to be "source shot noise limited".

The results of these theoretical considerations are presented in Table I, where calculated LOD values are listed for a number of different spectrometric methods. In Table I, AAL signifies atomic absorption measured with a line source (hollow cathode), AES denotes atomic emission spectrometry, and AFS is atomic fluorescence. Different atom reservoirs listed in the table are a chemical flame, an electrothermal atomizer (ETA), the ICP, and an MIP. When atomic fluorescence measurements are utilized, results are somewhat different when a xenon arc lamp (Xe) or laser are employed as excitation sources. For convenience, calculated LOD values are listed both in terms of solution con-

centration (ng/mL) or in terms of atoms/cm^3. Also, the calculated values are compared to experimentally realized LOD quantities for Na, Cu, and Pb.

Importantly, SAD feasibility exists among the methods mentioned in Table I only for atomic fluorescence generated by a laser and carried out in a carbon furnace atomizer. Moreover, this theoretical capability is not matched by experimental realization, as suggested earlier by the results of Bolshov, et al. (6). All other methods fall short of this capability. Only the microwave-induced plasma coupled with a microarc atomizer and atomic absorption employing a graphite furnace atomizer seem competitive with the atomic fluorescence method. Importantly, several of the analytical techniques listed in Table I exhibit experimental capability which already matches or approaches their theoretical limits, suggesting that little future improvements are to be expected.

Even for LEAF, detection capability for real samples falls far short of the SAD level. Table II lists a number of detection limits for different elements using LEAF in an electrothermal atomization device. Clearly, the example of lead cited earlier is an exception to the general trend of detection limits. For the sake of comparison, detection limits obtained by other atomic spectrochemical methods have been compiled in Tables III-V . Again, none of the methods approaches the SAD limit.

CONCLUSIONS

From Tables I-V it is clear that state-of-the-art methods of spectro-chemical analysis fall far short of single atom detection. In addition, from Table I it seems that many of the methods already approach their theo-

retical sensitivity limit. Therefore, it is unlikely that these methods will be extended to SAD in the future.

Of the various schemes which have been tried or proposed for SAD application, the most promising appears to be laser-excited atomic fluorescence (LEAF) using non-resonance transitions and saturation of energy levels. This method offers not only the requisite sensitivity for SAD, but enables each atom to be observed repeatedly, so that necessarily inefficient means for improving selectivity can be incorporated.

However, the key to practical ultra-high sensitivity atomic analysis lies in improvement of the methods for decomposing samples into their constituent atoms. Although thermal methods for atomization might be applicable to some samples and a few elements, new methods will have to sought. Of such methods, the most attractive one now available appears to be based on sputtering. To enhance the use of sputtering cells, it is proposed that atom-trapping or ion-trapping arrangements be considered. Alternatively, localized heating methods such as laser-induced ablation might be employed. Like sputtering, laser ablation erodes a sample from the outside, exposing successive atomic layers. Already, laser ablation has been coupled with resonance ionization spectroscopy (cf. Fig. 1) to yield a technique that is capable of detecting concentrations of atoms in localized sample regions of 10^{10}-10^{11} atoms/cm^3 (36).

It appears, then, that single-atom detection is not beyond the realm of analytical feasibility, even for real chemical samples. Although it will be some time, if ever, before SAD tools are routinely employed, one cannot avoid projecting the possible impact on analytical laboratories, record keeping, and governmental regulations. Ordinarily, even solvents purified by heroic means contain elemental concentrations above those listed

in Tables I- V . Moreover, with SAD capability, a "zero-pollution limit"
would become a verifiable, unrealistic, and not altogether desirable concept.

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Table I. DETECTION LIMITS - ATOMIC METHODS

Method	Limiting Noise Source	Calculated(23) ng/mL	Calculated(23) atoms/cm³	Detection Limits (ng/mL)[a]		
				Na Exptl.	Cu Exptl.	Pb Exptl.
AAL-flame	Source shot	1	10^8	0.4(37)	2(37)	20(37)
AAL-ETA	Source shot			4×10^{-3}(37)	5×10^{-3}(37)	7×10^{-3}(37)
AES-ICP 300 nm	Background shot	10^{-2}	10^5		0.06(38)	1(39)
600 nm		10^{-3}	10^4	0.1(38)		
AES-MIP				10^{-3}(24)	0.2(40)	0.4(24)
AFS-Xe	Background shot	10	10^9	8(41)	2(42)	10(42)
AFS-flame-laser	Background shot	10^{-3}	10^5	10^{-3}(8)	1(43)	13(43)
AFS-ETA-laser	Detector shot	10^{-8}	10^0	2×10^{-2}(7)	2×10^{-3}(7)	2.5×10^{-5}(7)

[a]Literature citations given in parentheses

Table II. Detection Limits by LEAF[a] in a Carbon Furnace Atomizer[b]

Element	Excitation Wavelength (nm)	Fluorescence Wavelength (nm)	Detection Limits (ng/L)	Detection Limits (pg)
Ag	328.1	338.3	3	0.1
Co	304.4	340.5	2	0.06
Cu	324.7	510.5	2	0.15
Eu	287.9	536.1	10^4	300
Fe	296.7	373.5	1	0.1
Ir	295.1	322.1	200	6
Mn	279.5	279.5	6	0.2
Na	589.6	589.6	20	0.6
Pb	283.3	405.7	2.5×10^{-2}	1.5×10^{-3}
Pt	293.0	299.7	4×10^3	120

[a] Laser-Excited Atomic Fluorescence.

[b] Taken from ref. 7.

Table III. Detection Limits of Several Elements by Inductively
Coupled Argon Plasma Emission Spectroscopy

Element	Emission Wavelength (nm)	Detection Limit (ng/mL)	Reference
Ag	328.07	1	(44)
Co	238.89	0.1	(38)
Cu	327.40	0.06	(38)
Eu	381.97	0.06	(45)
Fe	259.94	0.09	(46)
Ir	322.1	70	(39)
Mn	257.61	0.01	(38)
Na	588.99	0.1	(38)
Pb	220.35	1	(39)
Pt	265.95	0.9	(39)

Table IV. Detection Limits of Several Elements by Microwave-
Induced Plasma Emission Spectroscopy

Element	Emission Wavelength (nm)	Plasma Support Gas	Detection Limit (ng/mL)	Reference
Ag	328.07	Ar	0.16	(24)
Co	345.35	Ar	1[a]	(47)
Cu	327.40	Ar	0.16	(24)
Fe	373.49	Ar	1[a]	(47)
Mn	279.5	He	0.46	(25)
Na	589.6	Ar	0.001	(24)
Pb	216.9	Ar	0.38	(24)
Pt	265.95	Ar	110	(24)

[a]Sample introduced as volatile metal chelate.

Table V. Detection Limits of Several Elements
by Electrothermal Atomization Atomic
Absorption Spectroscopy[a]

Element	Absorption Wavelength (nm)	Detection Limit (ng/mL)
Ag	328.1	0.001
Co	240.7	0.008
Cu	324.7	0.005
Fe	248.3	0.01
Ir	208.8	0.5
Mn	279.5	0.0005
Na	589.0	0.004
Pb	217.0	0.007
Pt	265.9	0.2

[a]All values taken from reference 37.

Figure Captions

1. Energy-level diagrams illustrating the processes of Resonance Ionization Spectroscopy (RIS) and Laser Enhanced Ionization (LEI), sometimes termed the Opto-Galvanic Effect (OGE). Laser-induced transition is denoted L.

2. Diagrams showing various schemes for detection of atomic or ionic fluorescence. A fluorescence process is designated F, whereas a radiationless transition (quenching) is indicated by a wavy line.

3. Illustration of the effects of energy-level saturation (bleaching) on the populations of two atomic states. Diagram on left portrays laser-absorption (A) and stimulated emission (E). Figure on right indicates the effect of increasing laser power (irradiance) on the populations of upper (2) and lower (1) states.

4. Energy-level diagrams for simple absorption and emission events.

5. Sequence of events which ordinarily occurs to convert a chemical sample into free atoms or ions useful for single-atom detection. Top branch pertains to the events which occur in a typical flame or plasma; bottom branch refers to events in an electrothermal atomizer such as a carbon furnace.

6. Single-flash photograph of apparatus for studying atomization from single droplets in a flame. Droplet generator (left) injects a stream of 60-μm diameter droplets into a stable air-C_2H_2 flame (right) along a prescribed trajectory. (Photograph courtesy of R. E. Russo).

7. Schematic diagram of an inductively coupled plasma (ICP) and the quartz torch that supports it. See text for discussion. (Diagram courtesy of V. A. Fassel).

8. Conceptual illustration of sputtering of a conductive surface (below) by rare-gas ions.

9. Photograph of a "microarc" atmospheric-pressure sputtering discharge. The microarc can atomize quickly even non-conductive samples. The microarc cathode (left) has been coated with a dried sample containing Sr, Na, and Al. The anode (upper) has been ohmically heated to incandescence in order to stabilize the discharge.

10. Selectivity can be enhanced in laser-excited atomic fluorescence (LEAF) by employing a double-resonance or two-photon process. Here, the two photons, of different energy, are provided by lasers L_1 and L_2.

11. Scattered radiation can be distinguished from fluorescence through use of time-gating.

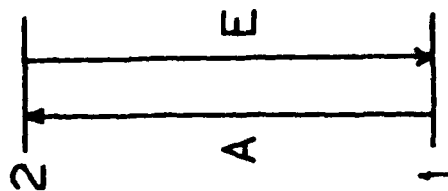Ionization Methods

RIS

LEI(OGE)

ionization level

thermal

2

1
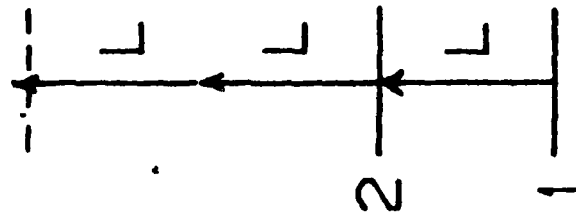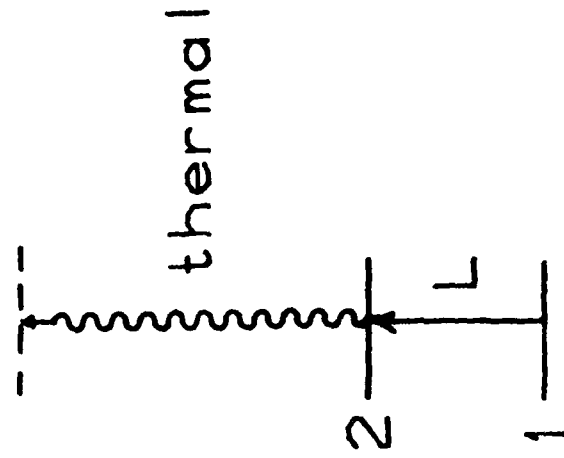
Fluorescence Methods
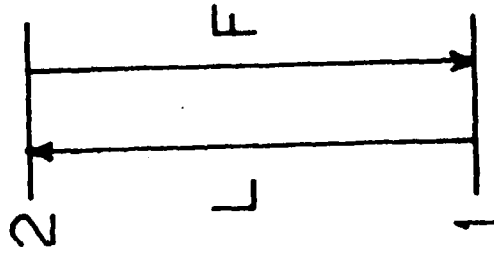
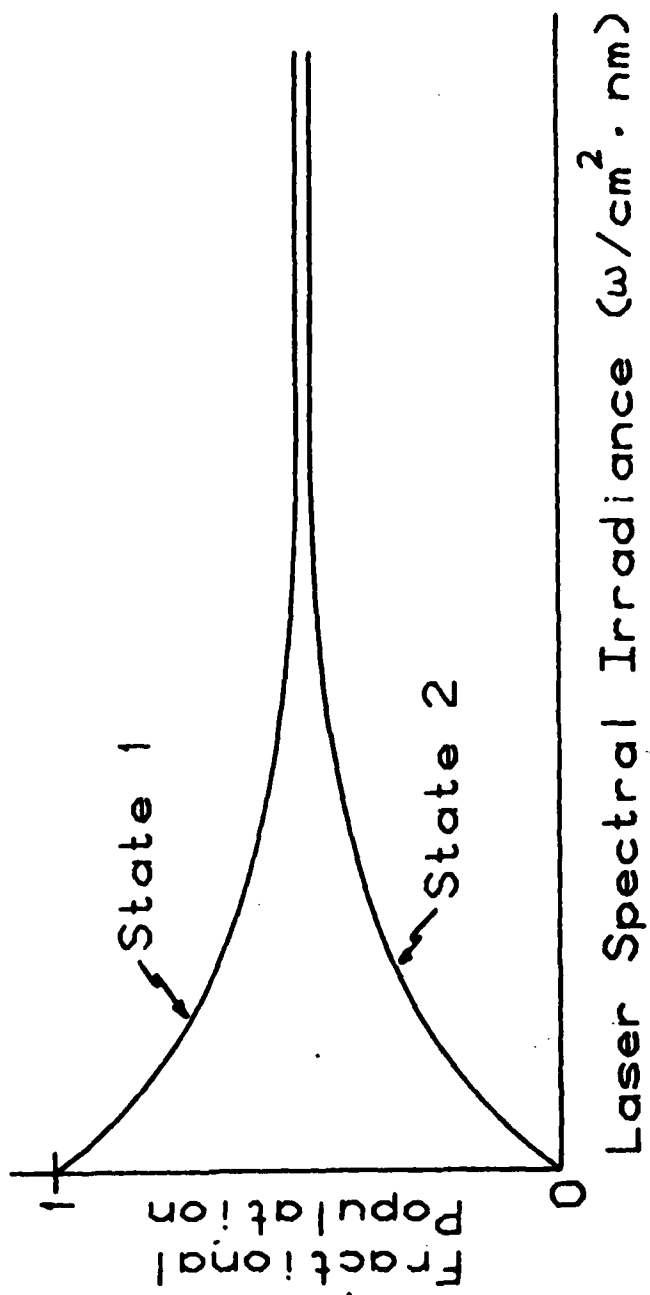Resonance   Direct Line   Stepwise

Saturation

Emission

2 ──────────────

                E
       ───────────────▶
   ◀∿∿∿∿∿∿∿∿∿∿∿∿

1 ──────────────

Absorption

2 ──────────────
   ◀──────────────
                A

1 ──────────────

ATOM PRODUCTION

ARGON
TANGENTIAL
COOLANT FLOW

ARGON
AND
SAMPLE AEROSOL

OPTIONAL
ARGON
FLOW

Sputtering

Ar^+

Ar^+

Ar^+

①

L_2

LEAF

L_1

C   SCATTERING

B   FLUORESCENCE

A   PHOTODIODE GATE

TIME →
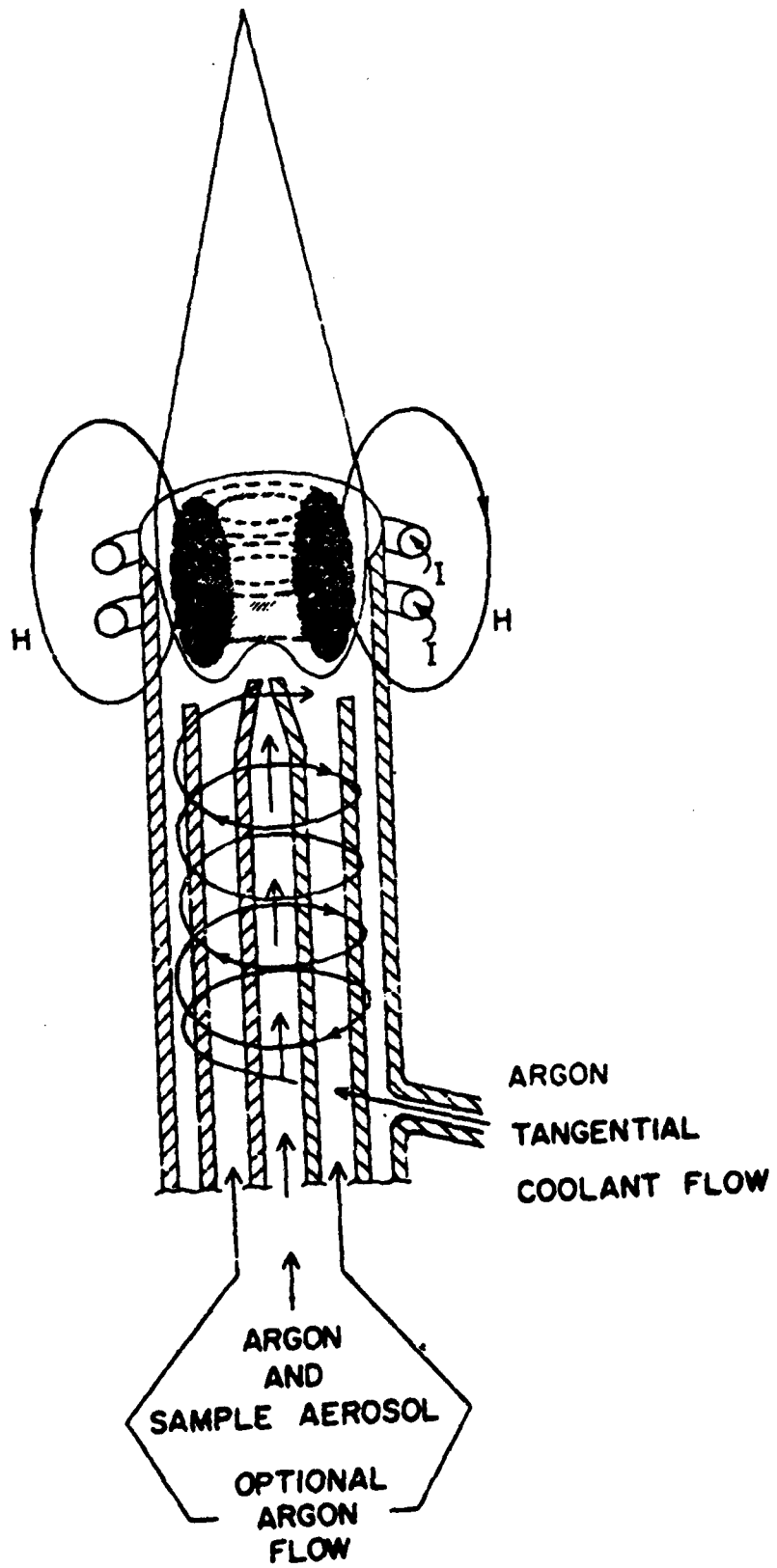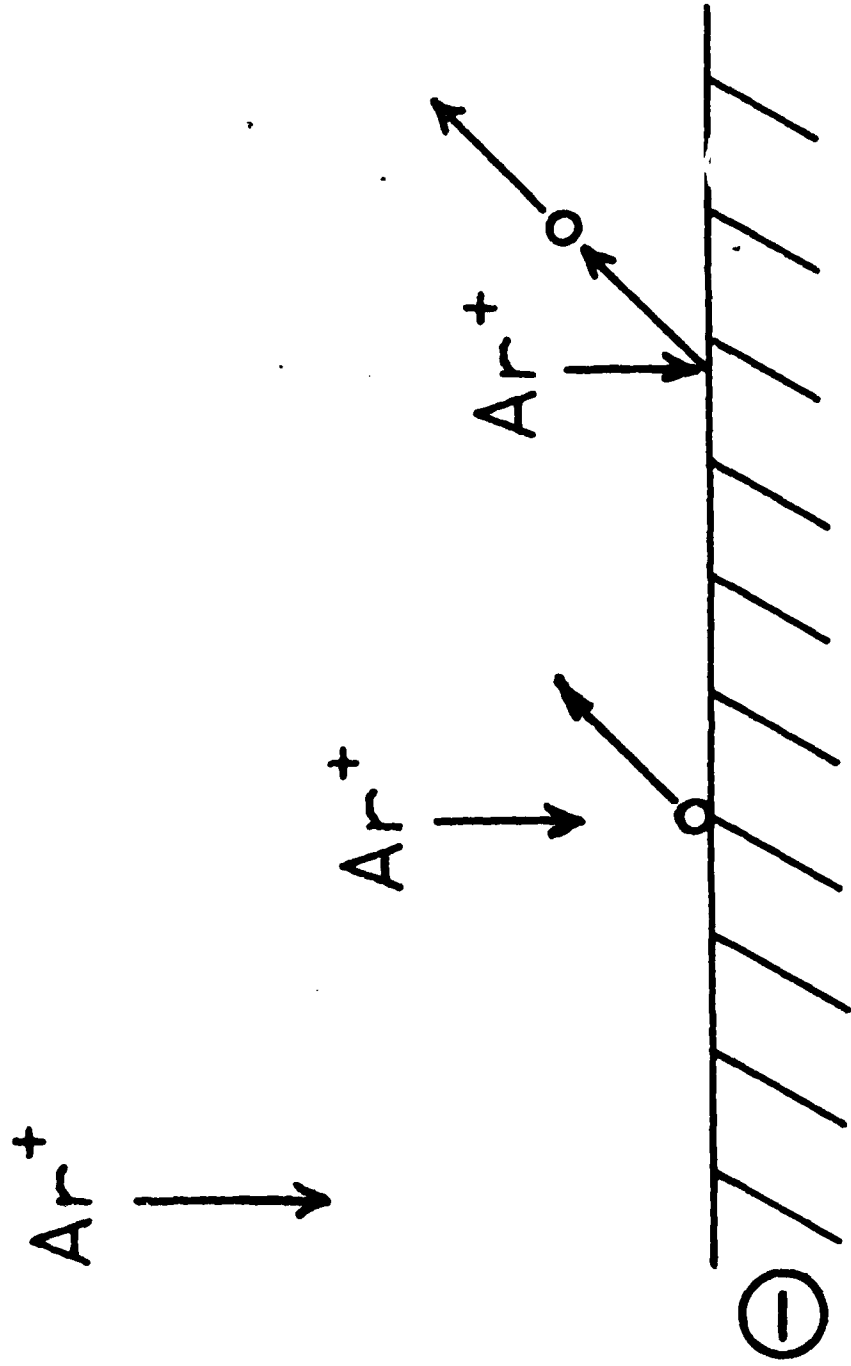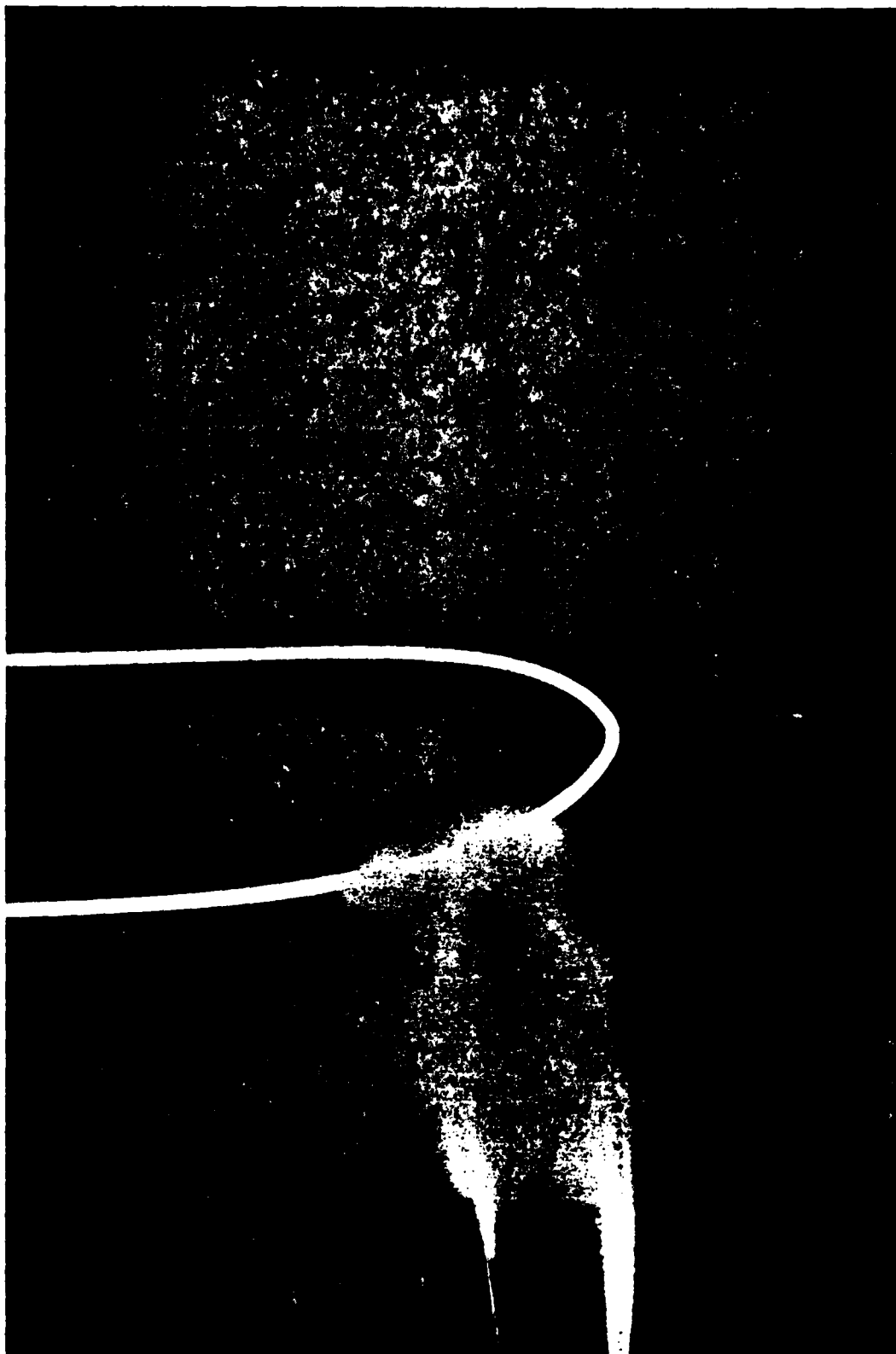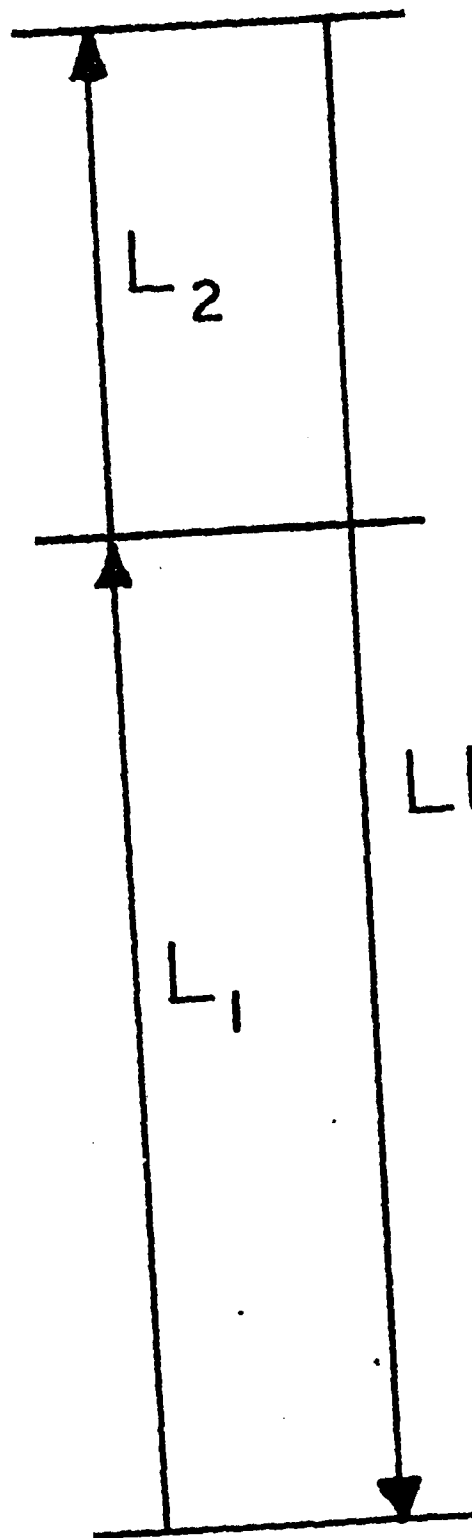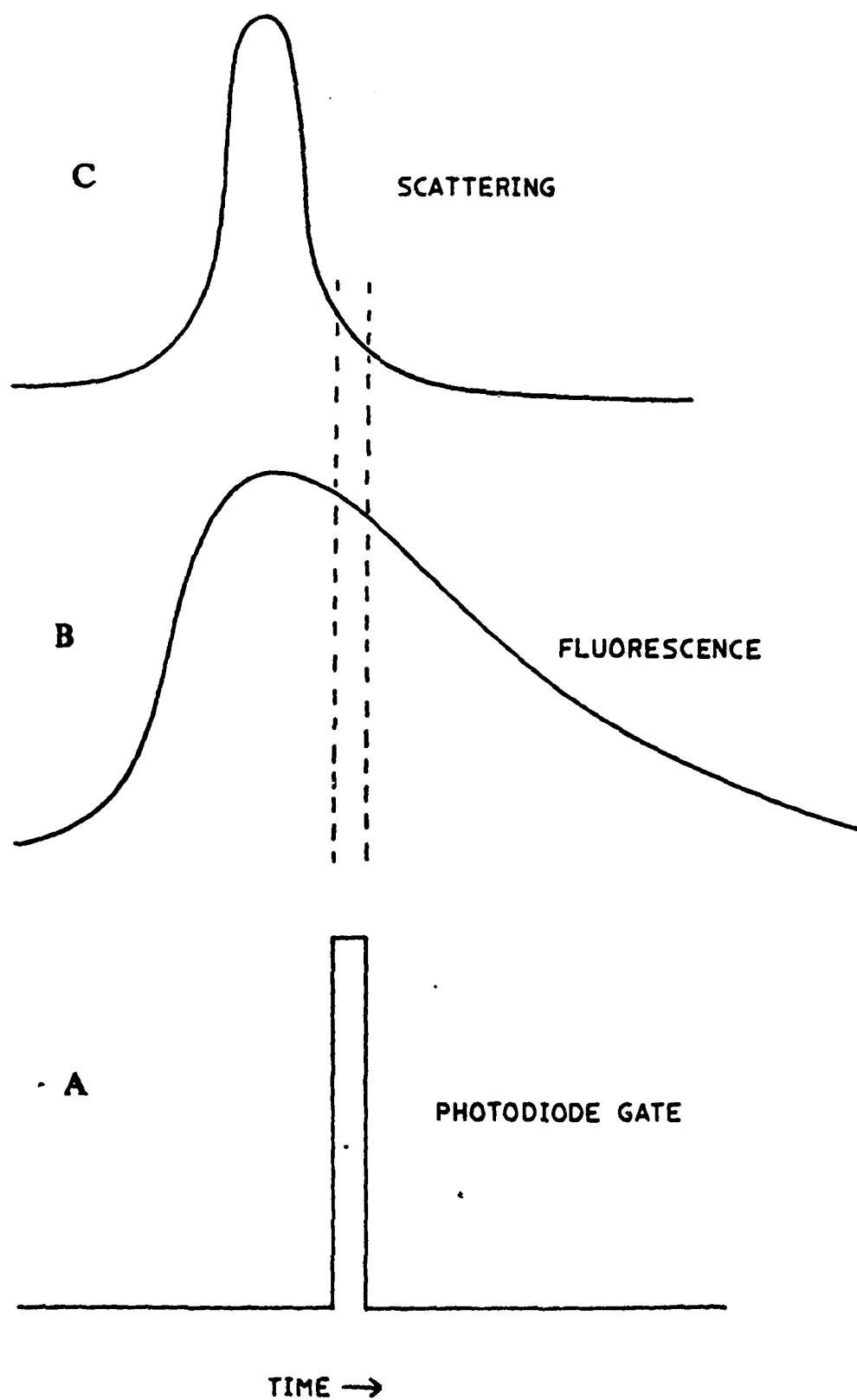
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